

# The role of electron-vibron interaction and local pairing in conductivity and superconductivity of alkali-doped fullerenes. The route to a room-temperature superconductor.

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We investigate the competition between the electron-vibron interaction (interaction with the Jahn-Teller phonons) and the Coulomb repulsion in a system with local pairing of electrons on the triply degenerate lowest unoccupied molecular orbital (LUMO). The electron-vibron interaction radically changes conductivity and magnetic properties of alkali-doped fullerenes  $A_nC_{60}$ , which should be antiferromagnetic Mott insulators: we have found that materials with  $n = 1, 2$  and  $A = K, Rb$  are conductors but not superconductors;  $n = 3$  and  $A = K, Rb$  are conductors (superconductors at low temperatures), but with  $A = Cr$  are Mott insulators;  $n = 2, 4$  are nonmagnetic Mott insulators. We have shown that superconductivity, conductivity and insulation of these materials have common nature. Based on the alkali-doped fullerenes we propose a hypothetical material with a significantly higher critical temperature using the model of superconductivity with the external pair potential formulated in a work *K.V. Grigorishin* arXiv:1605.07080 [cond-mat.supr-con].

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## I. INTRODUCTION

Alkali-doped fullerenes ( $A_nC_{60}$  with  $A = K, Rb, Cs$  and  $n = 1 \div 5$ ) demonstrate surprising properties. These materials are characterized with a narrow bandwidth  $W \sim 0.3 \div 0.5 \text{ eV}$  and a strong one-site Coulomb repulsion  $U \sim 0.8 \div 1.0 \text{ eV}$ . Moreover electrons on  $t_{1u}$  molecular orbital of fullerene should be distributed according to Hund's rule: spin of a molecule must be maximal. Thus alkali-doped fullerenes should be antiferromagnetic Mott insulators (the cases  $n = 0, 6$  a trivial: fullerene  $C_{60}$  has empty triply degeneracy  $t_{1u}$  conduction band and alkali-doped fullerene  $A_6C_{60}$  has the fully filled conduction band, hence these materials are band insulators). In reality the properties of the alkali-doped fullerenes are in striking contradiction to the expected properties. So  $A_2C_{60}$  and  $A_4C_{60}$  are nonmagnetic insulators. Thus molecule  $C_{60}$  with additional electrons in LUMO has not spin, that contradicts to Hund's rule. Under pressure these materials become metallic.  $A_1C_{60}$  and  $A_5C_{60}$  are conductors.  $A_3C_{60}$  is a superconductor with  $A = K, Rb$  for which the critical temperatures are sufficiently high  $T_c \sim 30 \text{ K}$ . However for  $A = Cr$  the material is insulators, but it becomes superconductors under pressure  $\sim 2 \text{ atm}$ . The mechanism of superconductivity of these superconductors has not been fully understood. The positive correlation between  $T_c$  and the lattice constant found in  $K$ - and  $Rb$ -doped fullerenes has been understood in terms of the standard BCS theory. Therefore superconductivity of  $A_3C_{60}$  is often described with Eliashberg theory in terms of electron-phonon coupling  $\lambda$  and Tolmachev's pseudopotential  $\mu^*$  [1–4]. However this material shows a surprising phase diagram [5], in which a high transition temperature of s-wave superconducting state emerges next to a Mott insulating phase as a function of the lattice spacing.

In the same time there is another approach to describe phases of alkali-doped fullerene - the model of local pairing [5–10]. The experimental basis for this hypothesis is the fact that the coherence length (size of a Cooper pair) in the superconducting alkali-doped fullerene is  $\sim 2 \div 3 \text{ nm}$ , which is comparable with a size of a fullerene molecule  $C_{60} \sim 1 \text{ nm}$ , that is a Cooper pair can localize on one molecule and it moves through lattice by hopping from site to site. In this model it suggests that the electron-vibron interaction (interaction with  $H_g$  and  $A_g$  intramolecular Jahn-Teller oscillations) favors the formation of a local singlet:  $\frac{1}{\sqrt{3}} \sum_m C_{im\uparrow}^+ C_{im\downarrow}^+ |0\rangle$ , where the spin-up and spin-down electrons is situated on a site  $i$  in the same quantum state  $m$ . Here  $|0\rangle$  is the neutral  $C_{60}$  molecule for the alkali-metal-doped materials, the quantum number  $m$  labels the three orthogonal states of  $t_{1u}$  symmetry. The local singlet state competes with the normal state (high spin state) of two electrons  $C_{im_1\uparrow}^+ C_{im_2\uparrow}^+ |0\rangle$  dictated by Hund's rule. Using this assumption it has obtained some important results. In a work [11] the density of states in a band originated from  $t_{1u}$  level has

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been calculated. It has been found that  $A_2C_{60}$  and  $A_4C_{60}$  are nonmagnetic semiconductors and the band gaps in these materials are cooperatively formed by the electron-electron and electron-vibron interactions. On the other hand,  $A_1C_{60}$ ,  $A_3C_{60}$  and  $A_5C_{60}$  are on the border of the metal-insulator transition. In a work [6] considering just the Hubbard model (the electron-vibron interaction is absent  $g = 0$ , the one-site Coulomb interaction takes place only), it is found that the metal-insulator transition in  $A_3C_{60}$  takes place at the upper range of what is believed to be physical values of  $U/W$ , while for  $A_4C_{60}$  this happens at the lower range of these parameters. This agrees nicely with the fact that  $A_3C_{60}$  is a metal but  $A_4C_{60}$  is an insulator. However, to explain why  $A_4C_{60}$  is not antiferromagnetic, it needs to include the coupling to the Jahn-Teller  $H_g$  phonons. The competition between the Jahn-Teller effect and the Hund's rule coupling increases  $U_c$  (critical value of the one-site Coulomb repulsion such that if  $U > U_c$  then a material is a Mott insulator) again. The coupling to the  $t_{1u}$  plasmons in  $A_3C_{60}$  should lead to an additional increase of  $U_c$  in this system. This makes that  $A_3C_{60}$  can be a metal.

In a work [7] it is shown that in  $A_3C_{60}$  the local pairing is crucial in reducing the effects of the Coulomb repulsion and overcoming the lack of retardation effects. So, for the Jahn-Teller  $H_g$  phonons the attractive interaction is overwhelmed by the Coulomb repulsion. Superconductivity remains, however, even for  $U_{vib} \ll U$ , and  $T_c$  drops surprisingly slowly as  $U$  is increased. The reason is in is as follows. For noninteracting electrons the hopping tends to distribute the electrons randomly over the molecular levels. This makes more difficult to add or remove an electron pair with the same  $m$  quantum numbers. However as  $U$  is large  $U > W$  the electron hopping is suppressed and the local pair formation becomes more important. Thus the Coulomb interaction actually helps local pairing. This leads to new physics in the strongly correlated low-bandwidth solids, due to the interplay between the Coulomb and electron-phonon interactions. In such system the Eliashberg theory breaks down because of the closeness to a metal-insulator transition. Because of the local pairing, the Coulomb interaction enters very differently for Jahn-Teller and non-Jahn-Teller models, and it cannot be easily described by a Coulomb pseudopotential:  $g - \mu^*$ . Theoretical phase diagram for  $A_3C_{60}$  systems has been obtained with the E-DMFT analysis in a work [5]. There are three phase: the superconducting phase at low temperature, the normal phase at more high temperatures and the phase of paramagnetic Mott insulator at bigger volume per  $C_{60}^{-3}$ . The s-wave superconductivity is characterized by a local order parameter  $\Delta = \sum_{m=1}^3 \langle C_{im\uparrow}^+ C_{im\downarrow}^+ \rangle$ , which describes intraorbital Cooper pairs for the  $t_{1u}$  electrons,  $m$  and  $i$  are the orbital and site(= molecule) indices respectively, the site index in  $\Delta$  is omitted because  $\Delta$  does not depend on a site (the solution is homogenous in space). Superconducting mechanism is that in such a system we have  $U' > U$  ( $U'$  is interorbital repulsion and  $U$  is intraorbital) due the electron-vibron interaction. Interesting observation is that the double occupancy  $\langle n_{m\uparrow} n_{m\downarrow} \rangle$  on each molecule increases toward the Mott transition and it jumply increases in a point of transition from the metal phase to the Mott insulator phase. Conversely, the double occupancy  $\langle n_{m\uparrow} n_{m'\downarrow} \rangle$  on each molecule and spin  $S$  per molecule decreases toward the Mott transition and they jumply decreases in the point of transition from the metal phase to the insulator phase (the spin changes from 3/2 to 1/2). These facts speak in favor of the local pairing hypothesis. The hypothesis is confirmed with quantum Monte Carlo simulations of low temperature properties of the two-band Hubbard model with degenerate orbitals [10]. It have been clarified that a superconducting (SC) state can be realized in a repulsively interacting two-orbital system due to the competition between the intra- and interorbital Coulomb interactions: it must be  $U < U'$ . This s-wave SC state appears along the first-order phase boundary between the metallic and paired Mott states in the paramagnetic system. On the other hand, the exchange interaction  $K$  destabilizes the SC state additionally.

In the Section II based on the local pairing hypothesis we propose a general approach to description of the properties of alkali-doped fullerides  $A_nC_{60}$  ( $A = K, Rb, Cs$ ,  $n = 1 \div 5$ ). We show that mechanism of superconductivity of  $A_3C_{60}$  (interaction with the Jahn-Teller phonons and the local pairing) uniquely determines conductivity of  $A_nC_{60}$  with  $n = 1, 3, 5$  and insulation of the materials with  $n = 2, 4$  with lack of antiferromagnetic properties. Thus superconductivity, conductivity and insulation of these materials have common nature. Obtained results can be used for increase of the critical temperature. In the Section III based on the alkali-doped fullerides we propose hypothetical material for realization of model of superconductivity with the external pair potential formulated in work [13]. In this model the energy gap tends to zero asymptotically as  $1/T$  with increasing of temperature. Formally the critical temperature of such superconductor is equal to infinity.

## II. THE MECHANISM OF CONDUCTIVITY AND SUPERCONDUCTIVITY

Let us consider alkali-doped fulleride  $A_nC_{60}$  ( $A = K, Rb, Cs$ ,  $n = 1 \div 5$ ). Due to the quasispherical structure of the molecule  $C_{60}$  the electron levels would be spherical harmonics with the angular momentum  $l$ , however the icosahedral symmetry generates the splits of the spherical states into icosahedral representation [14–16]. Fig.1 shows molecular levels close to the Fermi level. The LUMO is the 3-fold degenerate  $t_{1u}$ -orbital (i.e. it can hold up to six electrons). It is separated by about 2eV from the highest occupied molecular orbital (HOMO) and by about 1eV from the

next unoccupied level (LUMO+1). The alkali-metal atoms give electrons to the empty  $t_{1u}$  level so that the level becomes partly occupied. It should be noted that with spin-orbit coupling taken into account, the static Jahn-Teller configurations in the  $C_{60}^-$  molecule are unstable even in the limit of strong electron-vibron coupling and the symmetry of the atomic configuration of the unperturbed  $C_{60}$  molecule is restored under time averaging [17]. Hamiltonian of the system can be written in a form of three-orbital Hubbard Hamiltonian with the Hund coupling [10, 12] and the electron-vibron (Jahn-Teller phonons) interaction:

$$\begin{aligned}\hat{H} = & \sum_{\langle ij \rangle} \sum_m \sum_{\sigma} (t_{ijmm} + (\varepsilon_m - \mu)) a_{im\sigma}^+ a_{jm\sigma} + \frac{1}{2} U \sum_i \sum_m \sum_{\sigma} n_{im\sigma} n_{im-\sigma} \\ & + \frac{1}{2} (U' - K) \sum_i \sum_{m < m'} \sum_{\sigma} n_{im\sigma} n_{im'\sigma} + \frac{1}{2} (U' + K) \sum_i \sum_{m < m'} \sum_{\sigma} n_{im\sigma} n_{im'-\sigma} \\ & + \frac{1}{2} V \sum_{\langle ij \rangle} \sum_{mm'} \sum_{\sigma\sigma'} n_{im\sigma} n_{jm'\sigma'} + \hat{H}_{vib},\end{aligned}\quad (1)$$

where  $a_{im\sigma}^+$  ( $a_{im\sigma}$ ) is the electron creation (destruction) operator in the orbital  $m = 1, 2, 3$  localized at the site  $i$ ;  $n_{im\sigma} = a_{im\sigma}^+ a_{im\sigma}$  is the particle number operator;  $\sigma$  is the spin index;  $t_{ijmm}$  is the hopping integral between neighboring sites and the same orbitals;  $\varepsilon_m$  is the orbital energy (the energies can be supposed equal for all  $m$ );  $\mu$  is the chemical potential;  $U$  is the intra-orbital on-site Coulomb repulsion energy;  $U'$  is the inter-orbital on-site Coulomb repulsion energy;  $K > 0$  is the on-site exchange interaction energy:

$$U = \int d\mathbf{r} d\mathbf{r}' |\phi_m(\mathbf{r})|^2 V_c(\mathbf{r}, \mathbf{r}') |\phi_m(\mathbf{r}')|^2 \quad (2)$$

$$U' = \int d\mathbf{r} d\mathbf{r}' |\phi_m(\mathbf{r})|^2 V_c(\mathbf{r}, \mathbf{r}') |\phi_{m'}(\mathbf{r}')|^2 \quad (3)$$

$$K = \int d\mathbf{r} d\mathbf{r}' \phi_m^*(\mathbf{r}) \phi_{m'}^*(\mathbf{r}') V_c(\mathbf{r}, \mathbf{r}') \phi_m(\mathbf{r}') \phi_{m'}(\mathbf{r}), \quad (4)$$

where  $V_c(\mathbf{r}, \mathbf{r}')$  is a operator of on-site Coulomb interaction. Corresponding electron configurations shown in Fig.2. It should be noted that  $U \gg K$ ,  $U' \simeq U - 2K$  (the RPA interaction parameters taken from [5] is  $U \sim 0.82\text{eV}$ ,  $U' \sim 0.76\text{eV}$ ,  $K \sim 31\text{meV}$ ). Then  $U' - K < U' + K < U$  that means Hund's rule: the electron configuration with minimal energy has maximal spin. The energy  $V$  is the Coulomb repulsion between neighboring sites ( $i \neq j$ ):

$$V = \int d\mathbf{r} d\mathbf{r}' |\phi_m^i(\mathbf{r})|^2 V_c^{ij}(\mathbf{r}, \mathbf{r}') |\phi_{m'}^j(\mathbf{r}')|^2, \quad (5)$$

where  $V_c^{ij}(\mathbf{r}, \mathbf{r}')$  is a operator of cross-site Coulomb interaction. In the  $C_{60}$  molecule the electrons couple strongly to eight  $H_g$  and two  $A_g$  intramolecular Jahn-Teller phonons (electron-vibron interaction) [6, 7, 11]. The operator of the el.-vib. interaction has a form:

$$\hat{H}_{vib} = \lambda \sum_i \sum_{m \leq m'} \sum_{\sigma} \sum_{\nu} V_{mm'}^{(\nu)} a_{im\sigma}^+ a_{im'\sigma} (b_{i\nu}^+ + b_{i\nu}), \quad (6)$$

where  $\lambda$  is a coupling constant, the coupling matrices  $V_{mm'}^{(\nu)}$  are determined by icosahedral symmetry [6]. For the coupling to  $A_g$  phonons the matrix is diagonal with all the diagonal elements equal to unity, for the coupling to  $H_g$  phonons the matrix has both diagonal elements and nondiagonal elements. Vibrational energies for the  $A_g$  and  $H_g$  modes are within the limits  $\omega = 393 \div 2271\text{K}$  [1, 18, 19]. We can see that the adiabatic parameter in such a system is  $\omega/W \lesssim 1$  unlike the parameter in conventional metals where  $\omega/W \ll 1$ . Thus Migdal's theorem is violated in alkali-doped fulleride: the highest-order diagrams has to be counted for electron-phonon interaction. However for the multi-band Jahn-Teller phonons a strong reduction of the vertex diagrams occurs [4], that is Migdal's theorem is valid formally.

According to the model of superconductivity of  $A_3C_{60}$  [6–9] the dynamical Jahn-Teller effect (interaction with  $H_g$  intramolecular oscillations) favors the formation of a local singlet

$$\frac{1}{\sqrt{3}} \sum_m C_{m\uparrow}^+ C_{m\downarrow}^+ |0\rangle, \quad (7)$$

where the spin-up and spin-down electrons have the same  $m$  quantum number, i.e., a local pairing takes place. Here  $|0\rangle$  is the neutral  $C_{60}$  molecule, the quantum number  $m$  labels the three orthogonal states of  $t_{1u}$  symmetry (LUMO

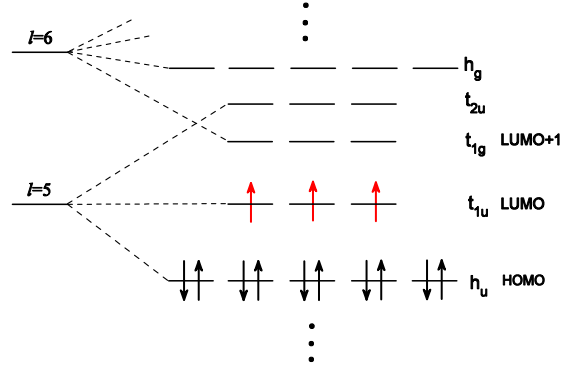


Figure 1: The molecular levels of  $C_{60}$  close to the Fermi level. In a substance  $A_3C_{60}$  the atoms of alkali metal  $A = K, Rb, Cs$  give electrons to the LUMO of the fullerene molecule (red color).

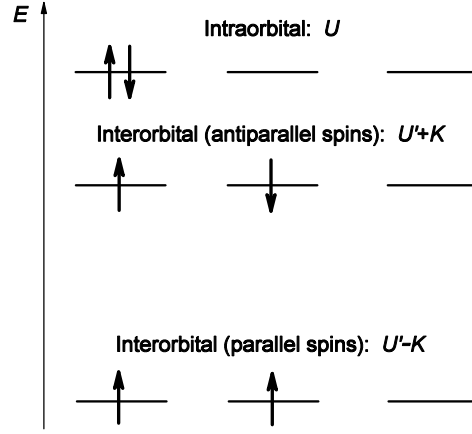


Figure 2: The electron configurations of two electrons on LUMO of a molecule  $C_{60}$ . Ground state corresponds to configuration with parallel spins. The intraorbital configuration has the largest energy.

state). In contrast, the normal state (high spin state) of two electrons is

$$\frac{1}{\sqrt{3}} \sum_{m_1 < m_2} C_{m_1 \uparrow}^+ C_{m_2 \uparrow}^+ |0\rangle. \quad (8)$$

As noted in [7], for noninteracting electrons the hopping tends to distribute the electrons randomly over the molecular levels. However if the on-site Coulomb repulsion  $U$  is large so that  $U > W$  the electron hopping is suppressed and the local pair formation becomes more important. Thus Coulomb interaction actually helps local pairing and superconductivity is result of interplay between the Coulomb blockade on a site and the hopping between neighboring sites. Superconductivity is expected to exist in this material right up to the Mott transition.

Based on the local pairing approach the Hamiltonian (1) can be simplified in the following manner. Fig.3 shows energies for different electron configurations of  $C_{60}^{-3}$  molecule (that is for the molecule in  $A_3C_{60}$  solid). We can see Hund's rule: the electron configuration with maximal spin  $S = 3/2$  has minimal energy:  $E_3 - E_1 = U - U' + 3K \simeq 5K > E_2 - E_1 = 4K > 0$ . Thus the ground state of the system is a state  $|m_1\sigma, m_2\sigma, m_3\sigma\rangle$ , in order to form a local pair (7) the energy  $E_3 - E_1 = U - U' + 3K$  must be expended. We can keep counting from the energy of this state, that is two electrons on a fullerene molecule "interact" with energy  $U - U' + 3K$  (the Hund coupling). Then we can reduce the Hamiltonian (1) to a form:

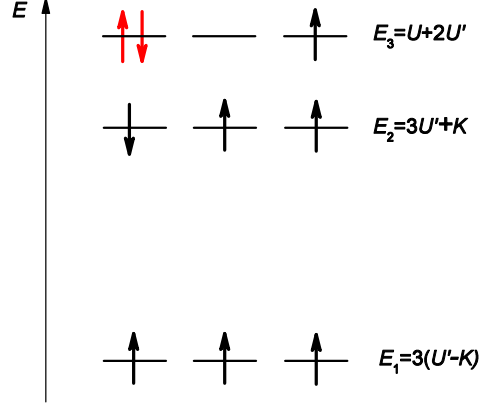


Figure 3: The electron configurations of three electrons on LUMO of a molecule  $C_{60}$ . Ground state corresponds to configuration with parallel spins. The configuration with a local pair (red color) has the largest energy.

$$\begin{aligned} \hat{H}_{eff} = & \frac{1}{2} (U' - K) \sum_i \langle n_i \rangle (\langle n_i \rangle - 1) + V \sum_{\langle ij \rangle} \langle n_i \rangle \langle n_j \rangle \\ & + \sum_{\langle ij \rangle} \sum_m \sum_{\sigma} (t_{ijmm} + (\varepsilon_m - \mu)) a_{im\sigma}^+ a_{jm\sigma} + \frac{1}{2} (U - U' + 3K) \sum_i \sum_m \sum_{\sigma} n_{im\sigma} n_{im-\sigma} + \hat{H}_{vib}, \end{aligned} \quad (9)$$

where  $\langle n_i \rangle$  is an average occupation number of a site  $i$ . The electron-vibron interaction can be reduce to BCS-like interaction (point, nonretarded) within single orbital  $m$  that corresponds to diagonal elements of the matrix  $V_{mm'}^{(\nu)}$ , and between different orbitals  $m$  and  $m'$  that corresponds to nondiagonal elements of the matrix. Then the Hamiltonian takes a form

$$\begin{aligned} \hat{H}_{eff} = & \sum_{\langle ij \rangle} \sum_m \sum_{\sigma} (t_{ijmm} + (\varepsilon_m - \mu)) a_{im\sigma}^+ a_{jm\sigma} \\ & + (U - U' + 3K - U_{vib}) \sum_i \sum_m n_{im\uparrow} n_{im\downarrow} - U'_{vib} \sum_i \sum_{m' \neq m} a_{im\uparrow}^+ a_{im'\uparrow} a_{im\downarrow}^+ a_{im'\downarrow}, \end{aligned} \quad (10)$$

where we omitted ground state energy (the first and second terms in Eq.(9)). We can distinguish the anomalous averages  $\langle a_{im\downarrow} a_{im\uparrow} \rangle$  and  $\langle a_{im\uparrow}^+ a_{im\downarrow}^+ \rangle$  in Eq.(10), then the Hamiltonian takes a following form:

$$\begin{aligned} \hat{H}_{eff} = & \sum_{\langle ij \rangle} \sum_{mm'} \sum_{\sigma} (t_{ij}^{mm} + (\varepsilon_m - \mu)) a_{im\sigma}^+ a_{jm\sigma} \\ & + \sum_i \sum_m \left[ \Delta_m^+ a_{im\uparrow} a_{im\downarrow} + \Delta_m a_{im\downarrow}^+ a_{im\uparrow}^+ \right] \\ & + (U_{vib} - U + U' - 3K) \sum_i \sum_m \langle a_{im\uparrow}^+ a_{im\downarrow}^+ \rangle \langle a_{im\downarrow} a_{im\uparrow} \rangle + U'_{vib} \sum_i \sum_{m' \neq m} \langle a_{im'\uparrow}^+ a_{im'\downarrow}^+ \rangle \langle a_{im'\downarrow} a_{im'\uparrow} \rangle \end{aligned} \quad (11)$$

where

$$\begin{aligned} \Delta_m = & \frac{U_{vib} - U + U' - 3K}{N} \sum_i \langle a_{im\downarrow} a_{im\uparrow} \rangle + \frac{U'_{vib}}{N} \sum_i \sum_{m' \neq m} \langle a_{im'\downarrow} a_{im'\uparrow} \rangle \\ \Delta_m^+ = & \frac{U_{vib} - U + U' - 3K}{N} \sum_i \langle a_{im\uparrow}^+ a_{im\downarrow}^+ \rangle + \frac{U'_{vib}}{N} \sum_i \sum_{m' \neq m} \langle a_{im'\uparrow}^+ a_{im'\downarrow}^+ \rangle \end{aligned} \quad (12)$$

is the order parameter.  $N$  is the number of lattice sites (number of the molecules). Eq.(12) means that the order parameter in such system is determined with the local pairing. We can see that in this model the exchange energy  $3K$

and difference  $U - U' \sim 2K$  resists the electron-vibron interaction  $U_{vib}, U'_{vib}$  in the local pairing. As indicated above the exchange energy  $K$  is much less than Coulomb repulsion  $U, U'$ . Thus for the local pairing a weaker condition  $U_{vib} \gtrsim 5K$  must be satisfied than  $U_{vib} \gtrsim U, V$ . The average number of electrons per site

$$\sum_m \langle n_m \rangle = \frac{1}{N} \sum_i \sum_m \sum_\sigma \langle a_{im\sigma}^+ a_{im\sigma} \rangle \quad (13)$$

is determined by the position of the chemical potential  $\mu$ , and  $\langle \dots \rangle = Z^{-1} \text{Tr} \dots \exp(-H/T)$  denotes averaging procedure where  $Z$  is a partition function and  $T$  is temperature.

The on-site Coulomb repulsions  $U, U'$ , the on-site exchange interaction energy  $K$  and the Coulomb repulsion between neighboring sites  $V$  determine the change of energy at transfer of an electron from a site to a neighboring site. This process is shown in Fig.4a. We can see that the energy change in this process is

$$\Delta E = E_2 - E_1 = U + 4K - V, \quad (14)$$

where  $E_1$  is energy of an initial electron configuration (the Hund's rule) of neighboring sites,  $E_2$  is energy of the configuration if to transfer one electron from the site to another. According to [20] a band conductor becomes insulator if

$$\frac{\Delta E}{W} > 1, \quad (15)$$

where  $W$  is a bandwidth. That is an electron has not enough reserve of kinetic energy to overcome the Coulomb blockade on a site. For example let us consider  $\text{K}_3\text{C}_{60}$ . According to [5]  $W = 0.502\text{eV}, U = 0.820\text{eV}, K = 31\text{meV}, V = 0.25\text{eV}$ , then  $\Delta E/W = 2.38$ . This means that  $\text{K}_3\text{C}_{60}$  would have to be the Mott insulator. However  $\text{K}_3\text{C}_{60}$  is conductor and, at low temperatures, is superconductor even.

Accounting of the el.-vib. interaction can change the situation. For the pair of electrons on a site in state, for example,  $m = 1$  we have from Eq.(10):

$$\begin{aligned} \hat{H}_{vib}(1 \leftrightarrow 1, 2, 3) = & - U_{vib} a_{1\uparrow}^+ a_{1\downarrow}^+ a_{1\downarrow} a_{1\uparrow} - U'_{vib} (a_{1\uparrow}^+ a_{1\downarrow}^+ a_{2\downarrow} a_{2\uparrow} + a_{2\uparrow}^+ a_{2\downarrow}^+ a_{1\downarrow} a_{1\uparrow}) \\ & - U'_{vib} (a_{1\uparrow}^+ a_{1\downarrow}^+ a_{3\downarrow} a_{3\uparrow} + a_{3\uparrow}^+ a_{3\downarrow}^+ a_{1\downarrow} a_{1\uparrow}). \end{aligned} \quad (16)$$

Thus each pair obtains energy  $-U_{vib} - 2U'_{vib}$  due interaction within own orbital  $1 \leftrightarrow 1$  with energy  $-U_{vib}$  and transitions into other two orbitals  $1 \leftrightarrow 2, 1 \leftrightarrow 3$  with energy  $-U'_{vib}$  for each. Formation of a local electron pair is possible if electron configuration with the pair has energy which is less than energy of electron configuration according to the Hund's rule (see Fig.3):  $U - U' + 3K - U_{vib} - 2U'_{vib} < 0$ . Then the change of energy at transfer of an electron from one site to the neighboring site is

$$\Delta E = E_2 - E_1 = U - V - U_{vib} - 2U'_{vib}, \quad (17)$$

as shown in Fig.4b. Here we can see more favorable situation for conductivity because  $\Delta E$  in this case is less than in a case of the Hund's rule configuration. Moreover the transfer of an electron creates a pair on the neighboring site. Then, as shown in Fig.4c, the pair can move from a site to a site without change of energy. Thus if the el.-vib. energy is such that  $\Delta E/W < 1$  then the material becomes conductor and superconductor at low temperatures.

We do not seek the parameters of el.-vib. interaction  $U_{vib}, U'_{vib}$  by microscopic calculation but we will determine them phenomenologically by the following method. Following a work [21], we can make transition from the site representation (11) to into the reciprocal (momentum) space with help of relations:

$$a_{\mathbf{k}m\sigma} = \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k}\mathbf{r}_j} a_{jm\sigma}, \quad a_{jm\sigma} = \frac{1}{\sqrt{N}} \sum_j e^{-i\mathbf{k}\mathbf{r}_j} a_{\mathbf{k}m\sigma}, \quad (18)$$

then we obtain the effective Hamiltonian like Hamiltonian of a multi-band superconductor:

$$\begin{aligned} \hat{H}_{eff} = & \sum_m \sum_{\mathbf{k}} \sum_{\sigma} \xi_m(k) a_{\mathbf{k}m\sigma}^+ a_{\mathbf{k}m\sigma} \\ & + \sum_{\mathbf{k}} \sum_m \left[ \Delta_m^+ a_{\mathbf{k}m\uparrow}^+ a_{-\mathbf{k}m\downarrow} + \Delta_m a_{-\mathbf{k}m\downarrow}^+ a_{\mathbf{k}m\uparrow}^+ \right], \end{aligned} \quad (19)$$

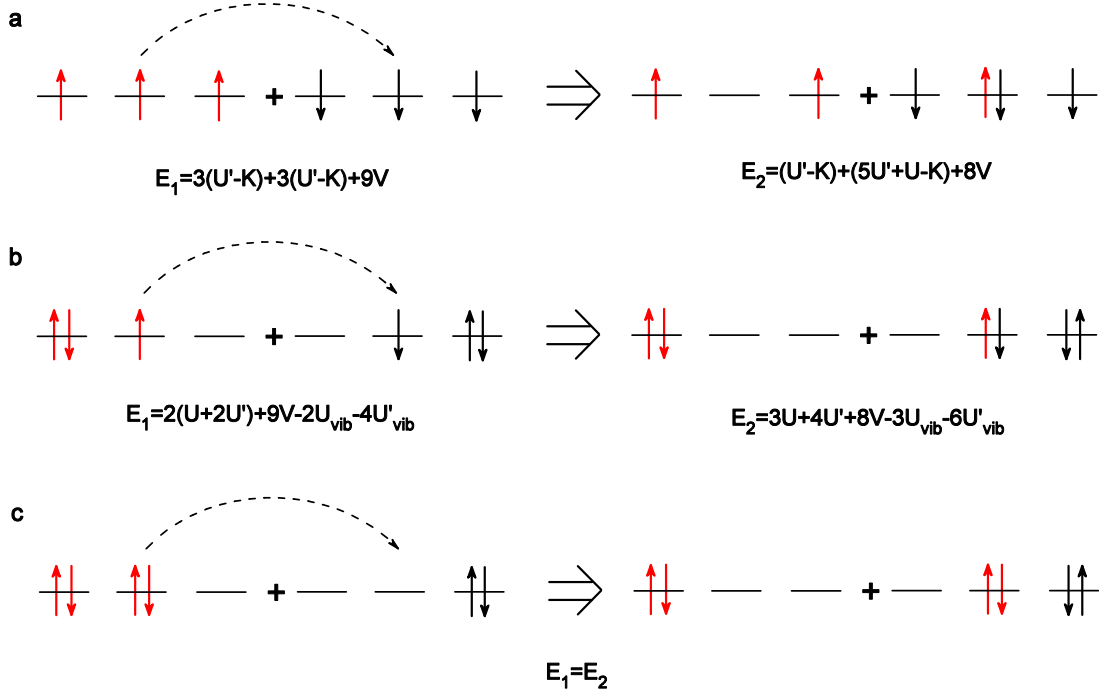


Figure 4: The transfer of a charge from a site to a neighboring site.  $E_1$  and  $E_2$  are the energies of the electron configurations before and after the transfer. (a) - the transfer of an electron without the el.-vib. interaction, (b) - the same but with the el.-vib. interaction which forms local pairs on sites, (c) - the transfer of a local electron pair.

with  $\xi_m(k) = \varepsilon_m(k) - \mu$ , and two last terms in Eq.(11) are omitted as a constant. The homogeneous equilibrium superconductivity gaps are defined as

$$\begin{aligned} \Delta_m &= \frac{U_{vib} - U + U' - 3K}{N} \sum_{\mathbf{k}} \langle a_{-\mathbf{k}m\downarrow} a_{\mathbf{k}m\uparrow} \rangle + \frac{U'_{vib}}{N} \sum_{\mathbf{k}} \sum_{m' \neq m} \langle a_{-\mathbf{k}m'\downarrow} a_{\mathbf{k}m'\uparrow} \rangle \\ \Delta_m^+ &= \frac{U_{vib} - U + U' - 3K}{N} \sum_{\mathbf{k}} \langle a_{\mathbf{k}m\uparrow}^+ a_{-\mathbf{k}m\downarrow}^+ \rangle + \frac{U'_{vib}}{N} \sum_{\mathbf{k}} \sum_{m' \neq m} \langle a_{\mathbf{k}m'\uparrow}^+ a_{-\mathbf{k}m'\downarrow}^+ \rangle, \end{aligned} \quad (20)$$

and the average number of electrons per site is

$$\sum_m \langle n_m \rangle = \frac{1}{N} \sum_{\mathbf{k}} \sum_m \sum_{\sigma} \langle a_{\mathbf{k}m\sigma}^+ a_{\mathbf{k}m\sigma} \rangle \quad (21)$$

Equations (20) and (21) should be solved self-consistently. It is easy to find that

$$\langle a_{-\mathbf{k}m\downarrow} a_{\mathbf{k}m\uparrow} \rangle = \frac{\Delta_m}{2E_m} \tanh \frac{E_m}{2T} \quad (22)$$

and

$$\langle a_{\mathbf{k}m\sigma}^+ a_{\mathbf{k}m\sigma} \rangle = \frac{1}{2} \left( 1 - \frac{\xi_m(k)}{E_m} \tanh \frac{E_m}{2T} \right), \quad (23)$$

where  $E_m = \sqrt{\xi_m(k)^2 + \Delta_m^2}$ . Thus a system with the local pairing  $\langle a_{im\downarrow} a_{im\uparrow} \rangle$  is equivalent to a multi-band superconductor with a continual pairing  $\langle a_{-\mathbf{k}m\downarrow} a_{\mathbf{k}m\uparrow} \rangle$  in each band.

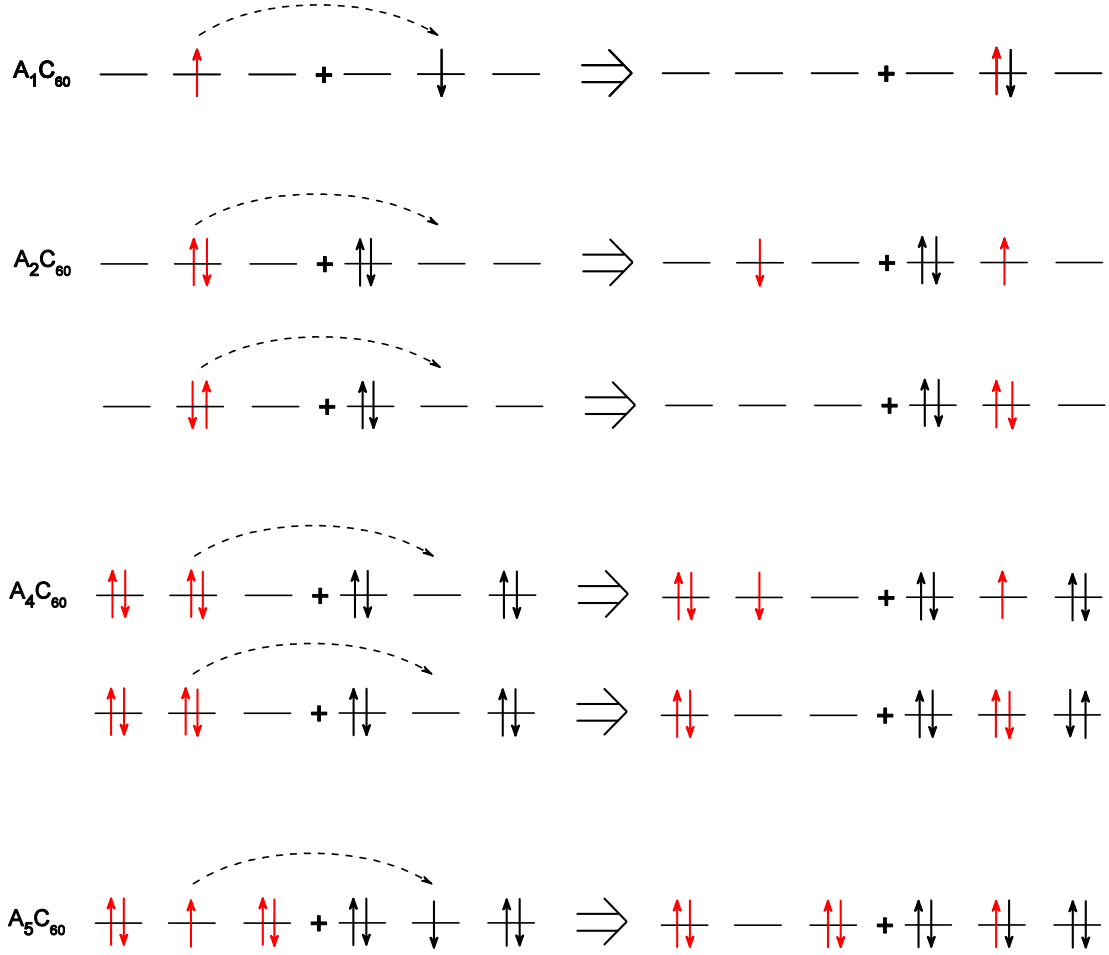


Figure 5: The charge transfer in materials  $\mathbf{A}_n\mathbf{C}_{60}$  where  $n = 1, 2, 4, 5$

The Eq.(20) can be simplified using effective phenomenological parameters. Namely, we can suppose  $U_{vib} = U'_{vib}$ . Dispersion low of electrons in  $t_{1u}$  conduction band  $\xi_m(k)$  is supposed the same for different orbitals  $m$ . Moreover we suppose the density of states in a branch  $m$  of the conduction band is a constant  $\nu = \nu_0$  if  $-W/2 < \xi < W/2$ , otherwise  $\nu = 0$ . Since  $\sum_{\mathbf{k}} \rightarrow V \int \nu(\xi) d\xi$  it is easy to show that

$$3 = \sum_m \langle n_m \rangle = 2 \frac{N}{V} \sum_m \int_{-W/2}^0 \nu_0 d\xi \Rightarrow \nu_0 = \frac{N}{V} \frac{1}{W}. \quad (24)$$

Then Eq.(20) is reduced to a form

$$\Delta = \frac{3U_{vib} - (U - U' + 3K)}{W} \int_{-\omega}^{\omega} \frac{\Delta}{2E} \tanh \frac{E}{2T} d\xi. \quad (25)$$

Thus we have an effective single-band superconductor with a coupling constant  $g$  determined with el.-vib. interaction  $3U_{vib}$ , and the Coulomb pseudopotential  $\mu$  determined with the Hund coupling  $U - U' + 3K$ :

$$g = \frac{3U_{vib}}{W}, \quad \mu = \frac{U - U' + 3K}{W}. \quad (26)$$

The therm  $3U_{vib}$  corresponds to the pair's binding energy  $-U_{vib} - 2U'_{vib}$  discussed above - Eq.(16). The parameter



$U_{vib}$  is chosen so that to obtain the experimental critical temperatures  $T_c$  of  $A_3C_{60}$ :

$$1 = (g - \mu) \int_{-\omega}^{\omega} \frac{1}{2\xi} \tanh \frac{\xi}{2T_c} d\xi. \quad (27)$$

The rest parameters  $W, U, U', K, V$  is taken from [5]. The bandwidth of alkali-doped fulleride is  $W \sim 0.5\text{eV}$ , the energy gap is  $\Delta = 1.764T_c \sim 30 \div 50\text{K} \ll \varepsilon_F = W/2$  that is a change of the chemical potential at transition to SC state can be neglected unlike the systems with the strong attraction and low particle density, where it can be  $\Delta > \varepsilon_F$  and the change of the chemical potential plays important role in formation of SC state [22]. On the other hand the vibrational energies for the  $A_g$  and  $H_g$  modes are  $\omega \sim 0.1\text{eV} \sim \varepsilon_F$  that means Tolmachev's weakening of the Coulomb pseudopotential by a factor  $\ln \frac{\varepsilon_F}{\omega}$  does not take place. In the same time for the multiband Jahn-Teller phonons a strong reduction of the vertex diagrams occurs [4], that is Migdal's theorem is valid formally.

The critical temperature  $T_c$  is calculated for the limit values of vibration energies of the intermolecular modes  $H_g$  and  $A_g$ . In addition we calculate the Mott parameter (15) for the state with local pairs (7) and for state without el.-vib. interaction where an electron configuration corresponds to the Hund's rule (8). Results of the calculations for  $A_3C_{60}$  (where  $A = K, Rb, Cr$  and the substance with cerium is considered at normal pressure,  $2\text{atm}$  and  $7\text{atm}$  with a lattice constant  $a$ ) are presented in the following table:

	K	Rb	Cr(7atm)	Cr(2atm)	Cr
$a(\text{\AA})$	14.240	14.420	14.500	14.640	14.762
$W(\text{eV})$	0.502	0.454	0.427	0.379	0.341
$U(\text{eV})$	0.82	0.92	0.94	1.02	1.08
$U'(\text{eV})$	0.76	0.85	0.87	0.94	1.00
$V(\text{eV})$	0.25	0.27	0.28	0.29	0.30
$K(\text{meV})$	31	34	35	35	36
$\frac{\Delta E}{W} = \frac{U+4K-V}{W}$	1.38	1.73	1.87	2.30	2.71
$T(\text{K})$	19	29	35	26	-
$U_{vib}(\text{eV})$ $\omega = 393\text{K}$ $\omega = 2271\text{K}$	0.104 0.085	0.113 0.091	0.114 0.092	0.106 0.89	$\sim 0.1$
$\frac{\Delta E}{W} = \frac{U-V-3U_{vib}}{W}$ $\omega = 393\text{K}$ $\omega = 2271\text{K}$	0.51 0.63	0.69 0.83	0.74 0.90	1.09 1.22	$\sim 1.4$

We can see that without the el.-vib. interaction we have  $\frac{\Delta E}{W} > 1$ , hence all materials are Mott insulators. The el.-vib. interaction changes the relation as  $\frac{\Delta E}{W} < 1$  for  $A=K, Rb, Cr$  (at  $7\text{atm}$ ), then these materials becomes conductors. We can see that the el.-vib. interaction  $U_{vib}$  is approximately constant  $\sim 0.1\text{eV}$  (that corresponds to  $g \sim 0.7$ ) at different lattice constants  $a$  and its value is such that  $U_{vib} > U - U', K$  but  $U_{vib} < U, U'$ . A material  $Cr_3C_{60}$  at pressure  $2\text{atm}$  is very close to Mott transition, hence our mean-field approximation is not correct due very strong fluctuations. For  $Cr_3C_{60}$  at pressure less  $2\text{atm}$  the el.-vib. interaction cannot ensure the condition  $\Delta E/W < 1$ , hence this material is a Mott insulator.

For understanding of properties of materials  $A_nC_{60}$ , where  $n = 1, 2, 4, 5$ , we can suppose that the el.-vib. interaction  $U_{vib}$  is approximately constant for these materials and is equal for the value in  $A_3C_{60} \sim 0.1\text{eV}$ , it is analogously for Coulomb  $U, U', V$  and exchange interactions  $K$ . The charge transfer in these materials is shown in Fig.5.

- $A_1C_{60}$ . In order to form a pair we have to transfer an electron from a site to a neighboring site containing another electron. For this it is necessary to make a positive work  $U - V - 3U_{vib} > 0$ . Thus formation of the pairs is energetically unfavorable. In the same time  $\frac{\Delta E}{W} = \frac{U-V-3U_{vib}}{W} < 1$ , however  $\frac{U-V}{W} \simeq \frac{U'-K-V}{W} \simeq \frac{U'+K-V}{W} > 1$  without the el.-vib. interaction. Thus this material is conductor due the el.-vib. interaction but it is not superconductor.
- $A_2C_{60}$ . Two electrons are in the paired state on a site because the energy of a paired state is  $U - U' - K - 3U_{vib} < 0$ . We can transfer the charge from site to site by two ways. (a) - by transferring one electron with breaking of a pair. In this case  $\frac{\Delta E}{W} = \frac{2U'-U-V+3U_{vib}}{W} > 1$ . (b) - by transferring the pair. In this case  $\frac{\Delta E}{W} = \frac{2U'-4V}{W} > 1$ . Thus this material is insulator and a molecule  $C_{60}^{-2}$  has not spin.
- $A_4C_{60}$ . Like the previous material four electrons are in the paired state on a site because the energy of a paired state is negative. We can transfer the charge from site to site by transferring one electron with breaking of pair and by transferring the pair. In these cases  $\frac{\Delta E}{W}$  is  $\frac{2U'-U-V+3U_{vib}}{W} > 1$  and  $\frac{2U'-4V}{W} > 1$  accordingly. Thus this material is insulator and a molecule  $C_{60}^{-4}$  has not spin.

- $A_5C_{60}$ . In order to transfer an electron from a site to a site we have to expend such energy that  $\frac{\Delta E}{W} = \frac{3U - 2U' - V - 3U_{vib}}{W} < 1$ . This process forms the pair which can move through the system, but  $3U - 2U' - V - 3U_{vib} > 0$  (energy of the pair is positive) that is the Cooper pairs are not stable. Thus this material is conductor due the el.-vib. interaction but it is not superconductor.

We can see the el.-vib. interaction transforms Mott insulators  $A_nC_{60}$  with  $n = 1, 3, 5$  to conductors. However for  $n = 2, 4$  this interaction prevents conduction and it pairs electrons within each molecules so that the molecules has not spin.

### III. THE MODEL OF A HYPOTHETICAL ROOM-TEMPERATURE SUPERCONDUCTOR.

In a work [13] the model of a hypothetical superconductor has been proposed. In this model an interaction energy between (within) structural elements of condensed matter (molecules, nanoparticles, clusters, layers, wires etc.) depends on state of Cooper pairs: if the pair is broken, then energy of the molecular system is changed by quantity  $v = E_a - E_b$ , where  $E_a$  and  $E_b$  are energies of the system after- and before breaking of the pair accordingly. Thus to break the Cooper pair we must make the work against the effective electron-electron attraction and must change the energy of the structural elements:

$$2|\Delta| \longrightarrow 2|\Delta| + v > 0. \quad (28)$$

The parameter  $v$  can be either  $v > 0$  or  $v < 0$  and in the simplest case it is not function of the energy gap  $|\Delta|$  ( $v = 0$  is a trivial case corresponding to BCS theory). Moreover it is supposed that  $v$  does not depend on temperature essentially like parameters of electron-phonon interaction. The condition  $2|\Delta| + v > 0$  ensures stability of the Cooper pairs (bound state of the electrons is energetically favorable), otherwise transformation (28) has not sense and such SC state can not exist. If  $v < 0$  then the breaking of a Cooper pair lowers energy of the molecular structure (or creation of the pair raises the energy). In this case the pairs become less stable. If  $v > 0$  then the breaking of the pair raises the energy (creation of the pair lowers the energy). In this case the pairs become more stable. The Hamiltonian corresponding to the transformations (28) is

$$\hat{H} = \hat{H}_{\text{BCS}} + \hat{H}_v = \sum_{\mathbf{k}, \sigma} \varepsilon(k) a_{\mathbf{k}, \sigma}^+ a_{\mathbf{k}, \sigma} - \frac{\lambda}{V} \sum_{\mathbf{k}, \mathbf{p}} a_{\mathbf{p}\uparrow}^+ a_{-\mathbf{p}\downarrow}^+ a_{-\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow} - \frac{v}{2} \sum_{\mathbf{k}} \left[ \frac{\Delta}{|\Delta|} a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+ + \frac{\Delta^+}{|\Delta|} a_{-\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow} \right], \quad (29)$$

where  $\hat{H}_{\text{BCS}}$  is BCS Hamiltonian: kinetic energy + pairing interaction ( $\lambda > 0$ ). The combinations  $a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+$  and  $a_{-\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow}$  are creation and annihilation of Cooper pairs operators. The field  $v$  is called as the *external pair potential*, since the potential is imposed on the electron subsystem by the structural elements of matter. The potential *essentially renormalizes the order parameter*  $\Delta$  which is determined from self-consistency equation:

$$\Delta = g \int_{-\omega}^{\omega} d\xi \frac{\Delta \left(1 + \frac{v}{2|\Delta|}\right)}{2\sqrt{\xi^2 + |\Delta|^2 \left(1 + \frac{v}{2|\Delta|}\right)^2}} \tanh \left( \frac{\sqrt{\xi^2 + |\Delta|^2 \left(1 + \frac{v}{2|\Delta|}\right)^2}}{2T} \right). \quad (30)$$

We can see that only the electron-electron coupling is the cause of superconductivity (if  $g \equiv \lambda \nu_F = 0$  then  $\Delta = 0$ ), but not the potential  $v$ . If  $v = 0$  we have the usual self-consistency equation in BCS theory. If  $v > 0$  then at large temperatures  $T \gg T_c(v = 0)$  the energy gap tends to zero asymptotically as  $1/T$  with increasing of temperature:

$$|\Delta| = \frac{g\omega v}{4T}. \quad (31)$$

Thus, formally, the critical temperature is equal to infinity, however the energy gap remains finite quantity - Fig.6.

In this work based on alkali-doped fulleride we propose realization of this model. As it has been show above, in this material a Cooper pair is formed on a molecule of size  $R = 3.55\text{\AA}$  as result a of the el.-vib. interaction and suppression of hopping between molecules by one-cite Coulomb interaction  $U$ . This situation is fundamentally different from superconductivity in metals, where the size of a Cooper pair is macroscopic quantity  $\sim 10^3 \div 10^4\text{\AA}$ . Let us consider some features of the molecular structure  $C_{60}$ . The Van der Waals radius of a carbon atom is  $R_W(\text{C}) = 1.70\text{\AA}$ . Thus a fullerene has an inner cavity in its center of size  $\Delta R = R(C_{60}) - R_W(\text{C}) = 1.85\text{\AA}$ . A noble gas atom X can be trapped in a carbon cage in the inner cavity (Fig.7) - we have an endohedral complex  $\text{X}@C_{60}$  [23–29]. Since for a helium atom

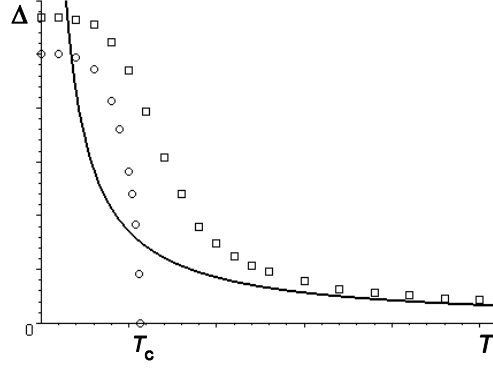


Figure 6: the energy gap as function of temperature. Circles are solutions of Eq.(30) if  $\nu = 0$  - standard result of BCS theory with the second order phase transition. Squares are solutions of Eq.(30) if  $\nu > 0$ . The solutions demonstrate, that the energy gap tends to zero asymptotically as temperature rises. Bold line is asymptotical solution (31) at large temperature.

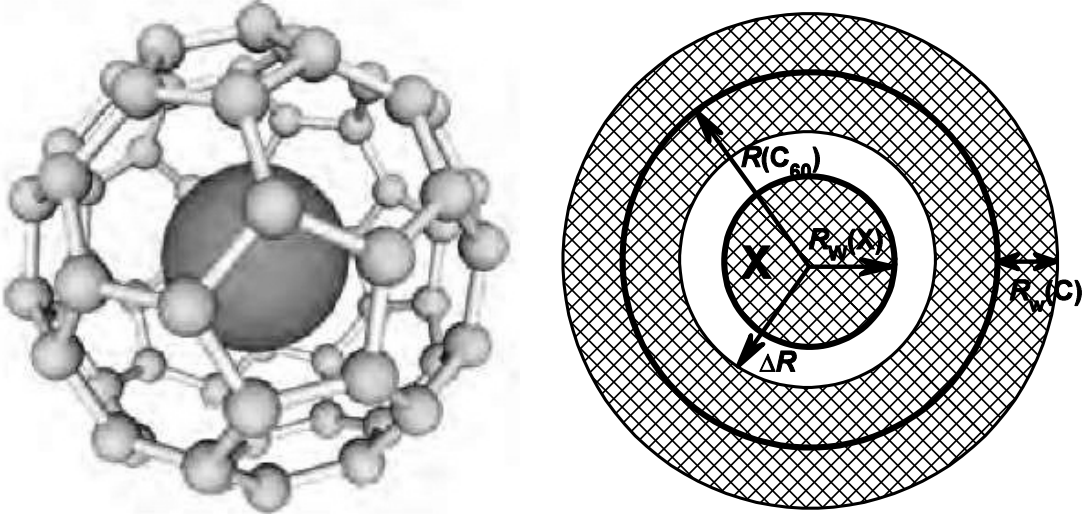


Figure 7: An endohedral fullerene  $X@C_{60}$  and cross-section of the endohedral fullerene. The carbon cage can be considered as a spherical layer of thickness  $2R_W(C)$  and central radius  $R(C_{60})$ . The central atom  $X$  placed into the inner cavity of radius  $\Delta R$  is a noble gas atom of Van der Waals radius  $R_W(X)$ .

$R_W(He) = 1.40\text{\AA} < \Delta R$  it's electronic shell does not make hybridized orbitals with electronic shells of the carbon cage. If helium atoms are placed into each fullerene molecule in alkali-doped fulleride then we have a hypothetical material  $A_3He@C_{60}$ . Electronic properties of  $A_3He@C_{60}$  must be identical to electronic properties of  $A_3C_{60}$ . Changes in oscillation spectrum of a fullerene can be neglected.

As noted above, in the endohedral fullerene the helium atom is trapped in a carbon cage and it interacts with the cage by Van der Waals force because  $R_W(He) < \Delta R$ . The carbon cage is barrier of width  $2R_W(C) + 2R_W(He)$  for the helium atom and there is the well of width  $2\Delta R - 2R_W(He) = 0.9\text{\AA}$  in the center of fullerenes - Fig.8. Let depth of the well is  $W \sim 70\text{meV}$  [23] and oscillation frequency (the average distance between energy levels) of the trapped helium atom is  $\Omega \sim 60 \div 120\text{cm}^{-1}$ . Van der Waals interaction depends on electron configuration of interacting subsystems (polarizability depends on the electron configurations). In alkali-doped fullerenes the alkali metal atoms give valent electrons to fullerene molecules. Then the interaction of the trapped helium atom with the carbon cage can depend on

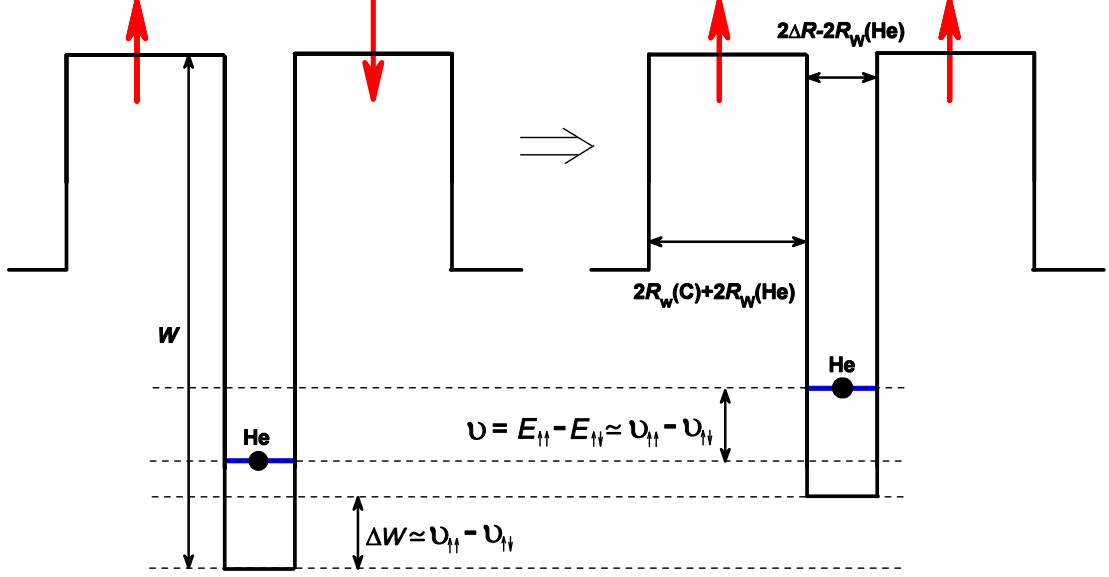


Figure 8: Process of breaking of an electron pair localized on a endohedral fullerene  $\text{He}@C_{60}$ . The process is accompanied by change of energy of a central helium atom  $E_{\uparrow\uparrow} - E_{\uparrow\downarrow} \simeq v_{\uparrow\uparrow} - v_{\uparrow\downarrow}$  (if  $\Delta W \ll W$ ).

a state of the excess electrons on the surface of a molecule  $C_{60}$ . Any two excess electrons can be in the paired state (7) or in the normal state (8). Let the interaction energy for the paired state is  $v_{\uparrow\downarrow}$  and the energy for the normal state is  $v_{\uparrow\uparrow}$ . If  $v_{\uparrow\downarrow} < v_{\uparrow\uparrow}$  then a molecule  $X@C_{60}^{-n}$  has lower energy if the excess electrons are in the paired state than the energy if the electrons are in the normal state. If  $v_{\uparrow\downarrow}, v_{\uparrow\uparrow} \ll W$  then change of depth of the well is  $\Delta W \simeq v_{\uparrow\uparrow} - v_{\uparrow\downarrow}$  at breaking of the pair. If  $v_{\uparrow\downarrow}, v_{\uparrow\uparrow} \ll \Omega$  then change of the helium atom's energy is  $E_{\uparrow\uparrow} - E_{\uparrow\downarrow} \simeq v_{\uparrow\uparrow} - v_{\uparrow\downarrow}$ . Hence a function

$$v = v_{\uparrow\uparrow} - v_{\uparrow\downarrow} \quad (32)$$

plays role of the external pair potential. The Hamiltonian corresponding to such system is

$$\begin{aligned} \hat{H}_{eff} = & \sum_{\langle ij \rangle} \sum_m \sum_{\sigma} (t_{ij}^{mm} + (\varepsilon_m - \mu)) a_{im\sigma}^+ a_{jm\sigma} \\ & + (U - U' + 3K - U_{vib}) \sum_i \sum_m n_{im\uparrow} n_{im\downarrow} - U'_{vib} \sum_i \sum_{m' \neq m} a_{im\uparrow}^+ a_{im'\uparrow} a_{im\downarrow}^+ a_{im'\downarrow} \\ & - \frac{v}{2} \sum_i \sum_m \left[ \frac{\Delta}{|\Delta|} a_{im\uparrow}^+ a_{im\downarrow}^+ + \frac{\Delta^+}{|\Delta|} a_{im\downarrow} a_{im\uparrow} \right], \end{aligned} \quad (33)$$

which can be reduced to the Hamiltonian (29) (where  $\lambda = 3U_{vib} - U + U' - 3K$ ) in reciprocal (momentum) space with help of transitions (18) and the assumption  $U'_{vib} = U_{vib}$ .

The Van der Waals interaction is interaction due to virtual transitions of the Cooper pair's electrons from a triply degenerate level  $t_{1u}$  ( $l = 5$ ) to levels  $t_{1g}$  ( $l = 5$ ),  $h_g, t_{2u}, h_u$  ( $l = 6$ ),  $g_g, g_u, t_g$  ( $l = 7$ ), ..., where  $l$  is an orbital index for  $\pi$ -electrons (see Fig.1):

$$\Phi_{0\uparrow\downarrow} \equiv \Omega_{l=5,\gamma}(\mathbf{R}_1) \Omega_{l=5,\gamma}(\mathbf{R}_2) \longleftrightarrow \frac{1}{\sqrt{2}} [\Omega_{l,\gamma'}(\mathbf{R}_1) \Omega_{l=5,\gamma}(\mathbf{R}_2) + \Omega_{l=5,\gamma}(\mathbf{R}_1) \Omega_{l,\gamma'}(\mathbf{R}_2)] \equiv \Phi_{k\uparrow\downarrow}[*], \quad (34)$$

[\*]we should write the ground state wave function as  $\frac{1}{\sqrt{3}} \sum_{\gamma=1}^3 \Omega_{l=5,\gamma} \Omega_{l=5,\gamma}$ . Accordingly the excited state wave function  $\Phi_{k\uparrow\downarrow}$  will have more cumbersome form. We suppose that results of calculations do not depend on the quantum index  $\gamma$  (that will be confirmed with the further calculations). Hence for convenience we can write the ground state wave functions in forms (34) and (38) fixing the index  $\gamma$ .

and of the helium atom from a level  $1s$  to levels  $2s, 2p, 3s, 3p, 3d, \dots$ :

$$\begin{aligned} \Psi_0 &\equiv f_{1,0}(r_1)Y_{0,0}(\mathbf{r}_1)f_{1,0}(r_2)Y_{0,0}(\mathbf{r}_2) \\ &\longleftrightarrow \frac{1}{\sqrt{2}} \left[ f_{n,\tilde{l}}(r_1)Y_{\tilde{l},\tilde{m}}(\mathbf{r}_1)f_{1,0}(r_2)Y_{0,0}(\mathbf{r}_2) + f_{1,0}(r_1)Y_{0,0}(\mathbf{r}_1)f_{n,\tilde{l}}(r_2)Y_{\tilde{l},\tilde{m}}(\mathbf{r}_2) \right] \equiv \Psi_p, \end{aligned} \quad (35)$$

where the index  $\gamma$  labels the irreducible representation of the icosahedral symmetry group;  $n, l, m$  are principal, orbital and magnetic quantum numbers accordingly;  $f_{n,l}(r)$  is a radial wave function,  $Y_{l,m}$  is a spherical wave functions.  $\Phi_0$  and  $\Psi_0$  are ground-states of a Cooper pair and a helium atom accordingly.  $\Phi_k$  and  $\Psi_p$  are the excited states of the Cooper pair and the helium atom accordingly,  $k$  and  $p$  are sets of quantum indices of the corresponding excited states.  $\mathbf{R}_1$  and  $\mathbf{R}_2$  are radius-vectors of electrons of the Cooper pair, and  $|\mathbf{R}_1| \approx |\mathbf{R}_2| \approx R$  since the Cooper pair is on surface of the molecule.  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are radius-vectors of electrons of the helium atom, and  $\langle r \rangle = 0.31\text{\AA} \ll R = 3.55\text{\AA}$  - the atom is much less than the fullerene molecule. Signs "+" in the sums are caused by the fact that the ground states of both the Cooper pair and the helium atom are singlet, and transitions between singlet and triplet states are allowed only due the spin-orbit interaction, but this interaction can be neglected. Energy of the Van der Waals interaction is defined with the second order correction:

$$v_{\uparrow\downarrow} = \sum_{k,p} \frac{|\langle \Phi_{k\uparrow\downarrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\downarrow} \rangle|^2}{E_0 + \tilde{E}_0 - E_k - \tilde{E}_p}, \quad (36)$$

where the summation is done over the indexes of all possible excited states of the Cooper pair  $k$  and of the helium atom  $p$ ;  $E_0$  and  $\tilde{E}_0$  are ground state energies of the Cooper pair and the helium atom accordingly,  $E_k$  and  $\tilde{E}_p$  are energies of the corresponding excited states. Since  $E_0 < E_k, \tilde{E}_0 < \tilde{E}_p$  then  $v_{\uparrow\downarrow} < 0$ . An operator of the interaction is

$$\hat{V}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}_1, \mathbf{r}_2) = \left( \frac{e^2}{|\mathbf{R}_1 - \mathbf{r}_1|} + \frac{e^2}{|\mathbf{R}_1 - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{R}_2 - \mathbf{r}_1|} + \frac{e^2}{|\mathbf{R}_2 - \mathbf{r}_2|} - \frac{2e^2}{|\mathbf{R}_1|} - \frac{2e^2}{|\mathbf{R}_2|} \right) / \varepsilon_\infty, \quad (37)$$

where  $\varepsilon_\infty \approx 5 \div 6$  [30] is the high-frequency dielectric function because the Van der Waals interaction is result of virtual transitions between atomic (molecular) levels (between molecular levels of  $\text{C}_{60}$  -  $\sim 3\text{eV}$ , between the levels of a helium atom -  $\sim 20\text{eV}$ ), while the plasma frequency in  $\text{A}_3\text{C}_{60}$  is  $\simeq 1.1\text{eV}$ . This is a very rough estimation of the screening, because the dielectric function is a continual characteristic of a medium, however we are dealing with intramolecular process. The problem of interaction of the trapped atom with the fullerene cage occupied additional electrons on LUMO in an alkali doped fulleride requires a separate study.

To calculate the energy of Van der Waals interaction if electrons are in the normal state (8) we can use an anti-symmetric wave function:

$$\begin{aligned} \Phi_{0\uparrow\uparrow} &\equiv \frac{1}{\sqrt{2}} [\Omega_{l=5,\gamma_1}(\mathbf{R}_1)\Omega_{l=5,\gamma_2}(\mathbf{R}_2) - \Omega_{l=5,\gamma_1}(\mathbf{R}_2)\Omega_{l=5,\gamma_2}(\mathbf{R}_1)] \\ &\longleftrightarrow \frac{1}{\sqrt{2}} [\Omega_{l,\gamma'}(\mathbf{R}_1)\Omega_{l=5,\gamma_2}(\mathbf{R}_2) - \Omega_{l,\gamma'}(\mathbf{R}_2)\Omega_{l=5,\gamma_2}(\mathbf{R}_1)] \equiv \Phi_{k\uparrow\uparrow}. \end{aligned} \quad (38)$$

Energy of the Van der Waals interaction is

$$v_{\uparrow\uparrow} = \sum_{k,p} \frac{|\langle \Phi_{k\uparrow\uparrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\uparrow} \rangle|^2}{E_0 + \tilde{E}_0 - E_k - \tilde{E}_p}. \quad (39)$$

It should be noted that due to electroneutrality of a helium atom and small size of the atom compared to radius of the molecule  $\langle r \rangle = 0.31\text{\AA} \ll R = 3.55\text{\AA}$  we have that  $\langle 00 | V | 00 \rangle = 0$  - the first order process can be neglected. We neglect the higher order processes, i.e. non-additivity of Van der Waals interaction. Moreover we can neglect the exchange processes between the helium atom and electrons on the molecule's surface, that cannot be done, for example, for atoms  $\text{Ar}$  and  $\text{Xe}$  due to overlap of the atom's wave functions with the wave functions of electrons of the fullerene cage [31–34].

Let us compare the energies  $v_{\uparrow\downarrow}$  and  $v_{\uparrow\uparrow}$ . To do this it is necessary to notice that the ground states of electrons on surface of a fullerene molecule have an important property. As well known

$$\langle \Omega_{l,\gamma} | \Omega_{l',\gamma'} \rangle = \delta_{ll'} \delta_{\gamma\gamma'}, \quad \langle f_{n,l} Y_{l,m} | f_{n',l'} Y_{l',m'} \rangle = \delta_{nn'} \delta_{ll'} \delta_{mm'}. \quad (40)$$

Then from Eq.(38) we can see that the high-spin ground state  $\Phi_{0\uparrow\uparrow}$  (normal state) is superposition of mutually orthogonal states with the weights  $1/\sqrt{2}$  each, unlike the low-spin ground state (paired state)  $\Phi_{0\uparrow\downarrow}$  - Eq.(34). We

have the following matrix elements:

$$\langle \Phi_{k\uparrow\downarrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\downarrow} \rangle = 2e^2 \int d\mathbf{R}_1 d\mathbf{r}_1 \frac{1}{|\mathbf{R}_1 - \mathbf{r}_1|} \Omega_{l,\gamma'}^+(\mathbf{R}_1) \Omega_{5,\gamma}^+(\mathbf{R}_1) f_{n,\tilde{l}}(r_1) Y_{l,\tilde{m}}^+(\mathbf{r}_1) f_{1,0}(r_1) Y_{0,0}(\mathbf{r}_1) / \varepsilon_\infty, \quad (41)$$

and

$$\langle \Phi_{k\uparrow\uparrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\uparrow} \rangle = \sqrt{2} e^2 \int d\mathbf{R}_1 d\mathbf{r}_1 \frac{1}{|\mathbf{R}_1 - \mathbf{r}_1|} \Omega_{l,\gamma_1'}^+(\mathbf{R}_1) \Omega_{5,\gamma_1}^+(\mathbf{R}_1) f_{n,\tilde{l}}(r_1) Y_{l,\tilde{m}}^+(\mathbf{r}_1) f_{1,0}(r_1) Y_{0,0}(\mathbf{r}_1) / \varepsilon_\infty, \quad (42)$$

where  $l \geq 5$  (if  $l = 5$  then  $\gamma'$  and  $\gamma_1'$  correspond to states in  $t_{2u}$  level - Fig.1),  $n > 1, \tilde{l} > 0$ ,  $d\mathbf{R} \equiv d\varphi \sin\theta d\theta$ ,  $d\mathbf{r} \equiv r^2 dr d\varphi \sin\theta d\theta$ . As noted above we have supposed that results of calculations do not depend on the quantum indexes  $\gamma, \gamma_1$  in the ground state wave functions. Hence we can fix  $\gamma$  by one of the indexes from  $t_{1u}$ . Let us determine the corresponding matrix elements assuming  $\gamma_1 = \gamma$  and  $\gamma_1' = \gamma'$  (the indexes  $l, \gamma', \gamma_1'$  run through all excited states by which the summation is done in Eqs.(36,39)). Then we have

$$\langle \Phi_{k\uparrow\downarrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\downarrow} \rangle = \sqrt{2} \langle \Phi_{k\uparrow\uparrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\uparrow} \rangle \quad (43)$$

for the corresponding matrix elements. Hence we obtain

$$v_{\uparrow\downarrow} = 2v_{\uparrow\uparrow}[*]. \quad (44)$$

Since the sign of Van der Waals interactions (36,39) is always negative  $v_{\uparrow\downarrow} < 0, v_{\uparrow\uparrow} < 0$ , then

$$v = -v_{\uparrow\uparrow} = -\frac{1}{2}v_{\uparrow\downarrow} > 0. \quad (45)$$

Thus an endohedral fullerene molecule  $\text{He}@C_{60}$  with excess electrons has a lower energy if the electrons are in the paired state (7) than energy if the electrons are in the state according to Hund's rule (8). This means that the potential  $v$  renormalizes the order parameter  $\Delta$  so that the asymptotic (31) occurs.

To estimate  $v$  a fullerene molecule can be considered as a sphere, that simplifies the calculation of the matrix elements (41,42). Then the wave functions on the fullerene's surface  $\Omega_{l,\gamma}$  are spherical wave functions  $Y_{l,m}$ . Ground state of an electron on the molecule is state with  $l = 5$ , which is degenerated in  $m = -l \dots l$ . The electron make virtual transitions to state with  $l = 6, 7, \dots$ . Energy of each level is

$$E_l = \frac{\hbar^2 l(l+1)}{2m_e R^2}, \quad (46)$$

that gives  $E_{5,m} - E_{6,m'} \approx 3.6\text{eV}$ . This value is order of distance between nearest molecular orbitals in a fullerene. For helium atom we have  $\tilde{E}_{1,0,0} - \tilde{E}_{n,\tilde{l},\tilde{m}} \approx 21\text{eV}$ . Calculation shows that  $v$  is almost independent of the quantum index  $m$ :

$$v_{\uparrow\downarrow}(m = 0 \dots \pm 5) \approx -80/\varepsilon_\infty^2 \text{K}, \quad (47)$$

hence  $v = -40/\varepsilon_\infty^2 \text{K}$ . For example, at  $T = 300\text{K}$  with help Eq.(31) we have  $\Delta \simeq 0.5\text{K}$ . However, as noted above the description of the screening with the dielectric function  $\varepsilon_\infty$  is a very rough estimation, because this function is a continual characteristic of a medium, however we are dealing with intramolecular process.

In connection with the obtained results it should be noted that in works [35, 36] it had been reported about the synthesis of the first endohedral fullerene superconductors  $\text{A}_3\text{Ar}@C_{60}$  having critical temperatures on 2 – 3 kelvins less than critical temperatures of the pure materials  $\text{A}_3C_{60}$ . The Van der Waals radius of Ar is  $R_W = 1.88\text{\AA}$  that is slightly more than radius  $\Delta R = 1.85\text{\AA}$  of the inner cavity in center of a fullerene molecule. In this case an overlap of the argon atom's wave functions with the wave functions of electrons of the fullerene cage occurs, hence the exchange interaction plays a role (the electron shell of a noble gas atom is embedded in the electron shell of fullerene) [31–34]. The radii of Kr and Xe are much larger, hence role of the exchange interaction is more significant. Thus the influence of Ar, Kr, Xe requires special consideration that goes beyond the present work. On the other hand, it should be noted that the Van der Waals radius of hydrogen molecule is  $R_W(\text{H}_2) \approx R_W(\text{H}) + R_{\text{COV}}(\text{H}) = 1.57\text{\AA} < \Delta R$ , where  $R_{\text{COV}}$  is a covalent radius. Thus the hydrogen molecule can be placed in the inner cavity of a fullerene without overlap of the electron shells like a helium atom. Hence the system  $\text{A}_3\text{H}_2@C_{60}$  can be similar to the system  $\text{A}_3\text{He}@C_{60}$ .

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[\*]we can select another  $\gamma_1 \neq \gamma$  but then we cannot determine the corresponding matrix elements with the relation (43) because  $\int d\mathbf{R}_1 \frac{1}{|\mathbf{R}_1 - \mathbf{r}_1|} \Omega_{l,\gamma'}^+(\mathbf{R}_1) \Omega_{5,\gamma}^+(\mathbf{R}_1) \neq \int d\mathbf{R}_1 \frac{1}{|\mathbf{R}_1 - \mathbf{r}_1|} \Omega_{l,\gamma_1'}^+(\mathbf{R}_1) \Omega_{5,\gamma_1}^+(\mathbf{R}_1)$  if  $\gamma_1 \neq \gamma, \gamma_1' \neq \gamma_1$ . However the relation  $v_{\uparrow\downarrow} \approx 2v_{\uparrow\uparrow}$  can be checked by direct calculation looking over all possible transitions.

#### IV. SUMMARY

We have reviewed conductivity and superconductivity of alkali-doped fullerenes  $A_nC_{60}$  ( $A = K, Rb, Cs$ ,  $n = 1 \div 5$ ) while these materials would have to be antiferromagnetic Mott insulators because interorbital Coulomb interaction is larger than bandwidth  $U \sim 1\text{eV} > W \sim 0.5\text{eV}$  and electrons on a molecule have to be distributed over molecular orbitals according to Hund's rule (8). We have found important role of the triply degeneracy of LUMO ( $t_{1u}$  level), small hopping between neighboring molecules and the coupling of electrons to Jahn-Teller modes. The coupling to Jahn-Teller modes  $U_{vib}$  cannot compete with interorbital Coulomb interaction  $U \gg U_{vib}$ , but it can compete with the Hund coupling  $U - U' + 3K \approx 5K \sim U_{vib}$  (where the exchange energy is much less than direct Coulomb interaction  $K \ll U$ ) due to the degenerate energy level  $t_{1u}$ . This allows to form the local pairs (a pair is formed on a molecule - Eq.(7)). The formation of local pairs and the coupling to Jahn-Teller modes radically change conductivity of these materials: they can make  $\frac{\Delta E}{W} < 1$ , where  $\Delta E$  is energy change at transfer of an electron from one site to neighboring site, while without accounting of the electron-vibron interaction we have  $\frac{\Delta E}{W} > 1$  that corresponds to Mott insulator. We have shown that  $A_1C_{60}, A_5C_{60}$  are conductors but not superconductors.  $A_3C_{60}$  is superconductor.  $A_2C_{60}, A_4C_{60}$  are Mott insulators but their fullerenes have not spin. This mechanism can ensure conductivity of  $A_3C_{60}$  if bandwidth is  $W \gtrsim 0.38\text{eV}$ , that is  $K_3C_{60}, Rb_3C_{60}$  are conductors (and superconductors) but  $Cr_3C_{60}$  is Mott insulator. We have shown that the system with the local pairing can be effectively described by BCS theory for multi-band superconductors. However in such system we have the effective coupling constant as  $g - \mu > 0$  (where  $g$  is determined with the el.-vib. interaction and  $\mu$  is determined with the Hund coupling - Eq.(26)) unlike usual metal superconductors where  $g - \mu^* > 0$  only (where  $\mu^*$  is a Coulomb pseudopotential with Tolmachev's reduction).

Based on the alkali-doped fullerene we have proposed realization of the model of superconductivity with the external pair potential formulated in [13]. In this model the potential essentially renormalizes the order parameter so that if the pairing lowers the energy of the molecular structure, then the energy gap tends to zero asymptotically as  $1/T$  with increasing of temperature - Eq.(31). Thus, formally, in this model the critical temperature is equal to infinity, however the energy gap remains finite quantity. For practical realization of this model we propose a hypothetical superconductor on the basis of alkali-doped fullerenes using endohedral structures  $He@C_{60}$ , where a helium atom is in the center of each fullerene molecule. In an endohedral fullerene the helium atom interacts with a carbon cage by Van der Waals force. The interaction depends on a state of excess electrons on surface of the molecule. We have shown that energy of the molecule if the excess electrons on its surface are in the paired state (7) (when two electrons are in a state with the same quantum numbers) is lower than the energy if the electrons are in the normal state (8) (when the electrons are in a state with different quantum numbers and maximal spin). Thus difference of the energies of the molecules plays a role of the external pair potential.

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